Kinetic Study of Supercritical Hydrothermal Synthesis of Organic-Modified Metal Oxide Nanoparticles and Process Proposal

アンジェイ　アレクサンダー　リドヴィノヴィッチ
氏　　名　Andrzej Alexander Litwinowicz
授　与　学　位　博士（工学）
学位授与年月日　平成２９年９月２５日
学位授与の根拠法規　学位規則第４条第１項
研究科，専攻の名称　東北大学大学院工学研究科（博士課程）　化学工学専攻
学 位 論 文 題 目　Kinetic Study of Supercritical Hydrothermal Synthesis of Organic-Modified Metal Oxide Nanoparticles and Process Proposal
（有機修飾金属酸化物ナノ粒子の超臨界水熱合成の速度論とプロセス提案）
指　導　教　員　東北大学教授　阿尻雅文
論 文 審 査 委 員　主査　東北大学教授　阿尻 雅文　東北大学教授　猪股　宏
東北大学教授　長尾　大輔　教授　高見　誠一
（名古屋大学大学院）
東北大学准教授　笘居 高明

論 文 内 容 要 旨

Chapter 1 Introduction

Nanomaterials have been studied intensely over recent years. Among the various suitable methods for nanoparticles (NPs) production [1] supercritical water (SCW) hydrothermal synthesis is a promising technology. This method combines the advantages of a clean and relatively efficient process for the production of nano-materials. Supercritical hydrothermal synthesis (SHS) of metal oxide NPs and their in-situ surface modifications with organic capping agents can create unique hybrid materials both, inorganic and organic properties [2].

Substantial efforts has been dedicated to understanding the formation mechanism of NPs and its kinetic behavior in sub- and supercritical hydrothermal conditions, this knowledge is necessary for rational reactor design [3-4]. Most relevant studies focused exclusively on the production of unmodified NPs. A kinetic study of metal oxide formation in the presence of surfactants was conducted, and the results were compared with those found for the formation of un-modified NPs, considering the effect of the solvent on the reaction. The results of this study are used to design a proposed process and, specifically, to evaluate the reactor size and, thus, the equipment cost of the process. The agglomeration behavior of modified NPs under reaction conditions can also affected by the solvent properties, and therefore, an understanding of this behavior is essential for designing the reaction atmosphere.

Chapter 2 Background of Research

Adschiri et al. investigated the kinetics of unmodified metal oxide formation in sub- and supercritical environments and assumed that the reaction rate can be expressed via a Born-type equation [5]. The reaction rate accelerates nonlinearly because the dielectric constant of water decreases at the evaluated temperatures. Because the reaction rate is fast, mixing reactor designs for plug flow reactors have been deeply investigated to improve the heat transfer and, thereby, optimize the size and size distribution of the particles [6]. Recent studies [7–8] have assumed that metal complexes of metal ions and surfactants are formed from the metal salt reactant and supplied surfactant before the crystallization reaction occurs. Those studies focused on the growth and shape control of the synthesized NPs. However, the formed intermediate can alter the reactivity of the metal source, and a kinetic study is required to evaluate the influence of the surfactant on the metal oxide formation rate.

The stabilization of dispersed NPs in solution has been intensively studied to avoid the agglomeration of primary particles at room temperature [9]. Surface coating via ex or in situ modification is a common approach to prevent aggregation [10]. In the in situ supercritical hydrothermal method, organic-modified CeO_2 oxide NPs have been synthesized using hydrophobic capping agents [11]. The synthesized NPs exhibited high dispersibility in organic solvents at room temperature, suggesting that no cluster formation occurred in the reaction atmosphere. In contrast, when hydrophilic bi-functional capping agents were used, clusters formed during the reaction, although the affinity of the resulting NPs was believed to be higher than that in the case of hydrophobic modification. Thus, a general understanding of cluster formation is required to predict the behavior of primary NPs and, thus, avoid their cluster formation.

Chapter 3 Kinetic study of metal complexes in hydrothermal condition

The kinetics of hydrophilic-modified CeO_2 formation in the presence of an amino acid has been investigated. Amino acids are supposed to form metal complexes in aqueous solution.

The experiments were performed with a lab-scale flow-type reactor [12]. An aqueous solution of $Ce(NO_3)_3$ (0.01 M)

containing L-glutamic acid at different concentrations was mixed with preheated water in a T-mixer to rapidly achieve the desired reaction conditions. The mixed stream was then quenched to room temperature after passing through an isothermal zone where the reaction temperature was kept constant. The operating pressure was 25 MPa. The concentration of unreacted Ce ion remaining after the reaction was analyzed by by inductively coupled plasma (ICP).

The hydrothermal synthesis reaction in the presence of L-glutamic acid was evaluated as a first-order reaction. Figure 1 shows the dependence of the reaction rate on the surfactant concentration. The formation of solid CeO_2 was suppressed by the ligand and decreased as the L-glutamic acid concentration increased.

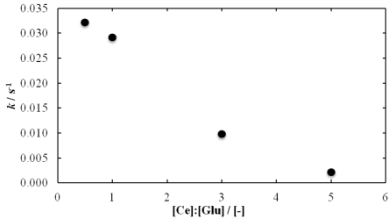


Figure 1. Reaction rate constant of the Ce ion dependence on the surfactant concentration (250°C, 25 MPa)

In water, complex formation occurs between the Ce ion and the amino acid via an equilibrium reaction; thus, increasing the L-glutamic acid concentration increases the formation of the complex in the precursor solution before the reaction. The activation energies (Figure 2) with and without different molar ratios of Ce to surfactant ([Ce]:[Glu]) were sufficient to be in the range required for a chemical reaction. The presence of the surfactant increased the activation energy. These results can be explained in terms of chemical potential of the reactant/intermediate species and the solvent effect: the complex formation decreases the chemical potential of the precursor solution and, thus, increases the activation energy because the reactant is more stable than the intermediates. Experiments with metal-oleate complex as a hydrophobic precursor were conducted to verify this assumption. As expected, the activation energy of the metal-oleate decreased relative to the metal salt reference; indeed, the chemical potential of the metal-oleate complex is higher in water because of its hydrophobic nature.

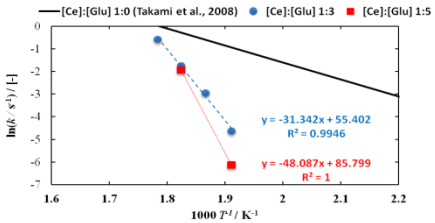


Figure 2. Arrhenius plot of CeO_2 formation without [12] and with surfactant (25 MPa)

Chapter 4 Organic-inorganic hybrid Nanoparticle agglomeration and dispersion behavior

The agglomeration behavior of CeO_2 NPs modified with L-glutamic acid was studied using the same experimental equipment as described in the previous section. The synthesis of crystalline CeO_2 was confirmed by X-ray diffraction (XRD). The spherical particle morphologies obtained in the presence of L-glutamic acid differs from that of unmodified octahedral CeO_2 nanocrystals. In addition, the calculated crystal size estimated from the XRD pattern of the products decreases as the initial amino acid concentration increases. This behavior indicates the interaction of the surfactant with the metal oxide surface and the suppression of crystal growth by the surfactant. Fourier transform infrared (FT-IR) and thermogravimetric (TG) analyses confirm the bonding of L-glutamic acid to the crystal phase by chemical absorption. The crystal size is ca. 18 nm, which differs from the particle sizes detected by transmission electron microscopy (TEM): 50 ~ 80 nm. This difference indicates cluster formation. TEM diffraction analyses and electron backscatter diffraction (EBSD) analysis of the cross section of the special cluster (synthesized at 275°C and 0.7 s) reveals that primary NPs have polycrystalline structures with different crystallographic orientations. As the reaction time increases, the particle shape becomes cubic (8 s), and the primary particles share the same crystallographic orientation (Figure 3). We suppose that the individual primary modified particles first loosely agglomerate to form a spherical cluster and then, in less than 4 s, order themselves into a 75-nm cubic mesocrystal to reduce the total surface energy via grain rotation. Hence, the behavior exhibited by primary particles forming a highly orientated mesocrystal is similar to that of molecules/monomers forming a crystal (Schema 1).

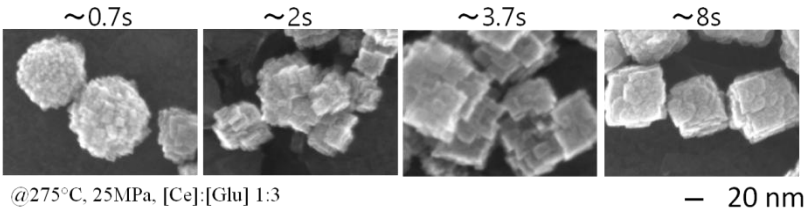
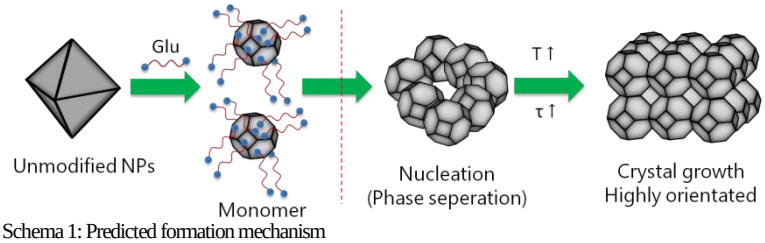


Figure 3. Evolution of CeO_2 clusters from polycrystals to mesocrystals

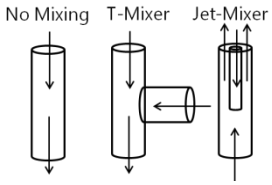
To confirm this assumption, experiments were conducted at 275°C and 0.7 s in which the solubility was decreased by adding ethanol ($x_{Ethanol}$ = 0.08) as an anti-solvent [13]. When the primary particle's solubility is lower, supersaturation increases, leading to smaller clusters. Hence, the solubility of the primary particle determines the formation of agglomerations (supersaturated) or dispersed modified NPs (not supersaturated). It can be assumed that the solubility of hydrophilic surfactants is lower under both sub- and supercritical conditions because of their lower dielectric and solubility parameters. Consequently, the primary CeO_2 NPs agglomerate. The dispersion or agglomeration of primary synthesized NPs in the reactor system can be predicted by evaluating the solubility of the modified NPs.



Schema 1: Predicted formation mechanism

Chapter 5 Proposal for in situ surface-modified NPs process

The product costs for the synthesis of NP via supercritical fluid technology with in situ modification and no modification were evaluated considering a production of 1,000 tons per year, which is comparable to the value for a commercial SHS plant [14]. For this comparison, the metal salt



Schema 2: Mixing reactor types

reactant, solvent, labor, and purification costs can be assumed to be the same and can, therefore, be omitted.

In the case of in situ modification, the reaction rate varies, and thus, the reactor size and cost also vary. For example, if the reaction rate increases relative to that of unmodified NP synthesis, as in the case of hydrophobic Co-oleate, the reactor size and cost will decrease.

In contrast, for the synthesis of hydrophilic CeO_2 mesocrystals under subcritical conditions, the reaction rate is approximately 5-fold lower, and therefore, a larger reactor size is needed. If the reactor cost is assumed to be 80% of the large capital equipment costs, applying the rule of 0.6 for the 5-fold scale-up of the reactor, the equipment cost increases by approximately 30%. In contrast, because the reaction rate is lower, the rapid mixing of the precursor with preheated water is not required. Therefore, a simplified reactor can be designed in which the water and precursor are mixed at room temperature and heated to the reaction temperature together (i.e., a no-mixing reactor type); this might reduce the equipment cost. More important is the total energy consumption for this system. The amounts of heat q required to achieve the reaction temperature $T_{Reaction}$ at 25 MPa using a no-mixing reactor, a T-mixer [12], and a Jet-mixer [3] were calculated assuming ΔT_{min} = 20°C [15] for the heat exchanger (Figure 4). The energy required for the no-mixing reactor was lower than those require for the mixing-type reactors because mixing a hot stream with a cold stream leads to a large exergy loss, and thus, high energy recovery cannot be achieved. The running cost can be decreased approximately 65–75% by using the no-mixing reactor at ΔT_{min} = 20°C. These results suggest that for the synthesis of surface-modified NPs with a lower reaction rate relative to the unmodified case, a no-mixing reactor is recommended.

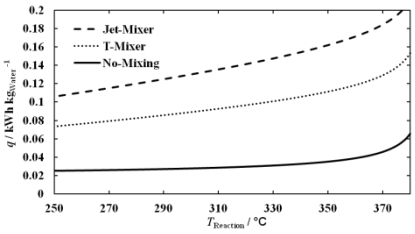


Figure 4. Energy per kg of water required to achieve the necessary reaction temperature using a no-mixing reactor, a T-mixer, and a Jet-Mixer at 25 MPa and ΔTmin = 20°C

Chapter 6 Summary

A kinetic study of a metal oxide in the presence of a surfactant was performed. The surfactant was observed to strongly influence the reaction rate, depending on the nature of the surfactant and its stability in the reaction solvent. Based on this study, the reaction rate of in situ-modified NP production can be predicted, and a suitable reactor, reactor size, and in situ modification process can be designed.

The formation mechanism of agglomerates and the evolution of mesocrystalline CeO_2 were observed and suggested that primary particles behave like molecules during crystallization.

The dispersion or agglomeration behavior can be predicted based on the solubility of the primary particle between the reaction and room temperatures. This prediction enables the recovery of dispersed single particles at the reactor outlet based on the solubility parameters of the surfactant and solvent.

Comparing the in situ modification and no-modification supercritical hydrothermal processes revealed that although the equipment cost increases, the running cost can be decreased by using a no-mixing reactor design. The energy savings compensate for the higher equipment cost associated with the in situ modification process. Thus, to synthesize surface-modified NPs with lower reaction rates, a no-mixing reactor is recommended.

Reference

[1] T. Tsuzuki, *Int. J. Nanotechnol.*, **6**, 567 (2009); [2] J. Zhang et al., *Adv. Mater.*, **19**, 203 (2007); [3] R. I. Gruar et al., *Ind. Eng. Chem. Res.*, **52**, 5270 (2013); [4] C. J. Tighe et al., *Ind. Eng. Chem. Res.*, **52**, 5522 (2013); [5] T. Adschiri et al., *J. Nanoparticle Res.*, **3**, 227 (2001); [6] L. Zhou, *Ind. Eng. Chem. Res.*, **53**, 481 (2014); [7] M. Taguchi et al., *RSC. Adv.*, **4**, 49605 (2014); [8] T. Fujii et al., *J. of Supercritical Fluid*, **118**, 148 (2016); [9] Y. Yin et al., *Nature*, **437**, 664 (2005); [10] B. Vincent et al., *J. Colloid Interface Sci.*, **73**, 508 (1980); [11] T. Arita, *Chem. Lett.*, **41**, 1235 (2012); [12] S. Takami et al., *Dalton Trans.*, **40**, 5442 (2008); [13] A. Cabañas et al., *J. of Supercritical Fluid*, **40**, 284 (2007); [14] T. Adschiri et al., Green Chem., **13**, 1380 (2013) [15] F. Marias, *Environ. Eng. Sci.*, **25**, 123 (2008).

論文審査結果の要旨

高分子や溶媒中にナノ粒子を高濃度分散させた有機無機ハイブリッド材料やナノ流体は、無機材料の有する諸物性（誘電、電気、磁気、光学、熱的特性）と成型加工性とを併せ持つ新たな機能性素材として、幅広い産業分野において開発が求められている。このようなナノ材料の開発にはナノ粒子表面の有機修飾が重要であり、その制御と大量処理法の開発が求められている。超臨界水は有機溶媒と均一相を形成し、ナノ粒子合成と同時に有機修飾を可能とすることから、有機修飾ナノ粒子の量産手法として期待される。

本研究は、有機修飾分子存在下における、金属酸化物ナノ粒子合成反応の速度論解析と、ナノ粒子の凝集挙動観察を通して、有機修飾金属酸化物ナノ粒子製造手法に適したプロセス提案を目指したもので、全６章から構成されている。

第１章は緒論であり、本研究の背景と目的を述べている。

第２章では、本研究に関連する既往の研究成果を調査し、本研究の狙いを明確にしている。

第３章では、有機修飾分子存在下における、金属酸化物ナノ粒子合成反応の速度論解析を行っている。特にＬ－グルタミン酸を修飾分子として用いた場合の反応速度、さらに活性化エネルギーについて詳細な検討を行っている。律速過程は、グルタミン酸と金属イオンから生成する錯体の加水分解にあり、その錯体の溶媒に対する親和性が、反応速度に及ぼす影響（溶媒効果）を実験と計算の両面から評価している。

第４章では、有機修飾分子存在下におけるナノ粒子の凝集挙動観察を行っている。Ｌ－グルタミン酸で修飾された酸化セリウムナノ粒子の合成反応場中での凝集挙動の時間変化を詳細に解析している。ナノ粒子があたかも１分子のように振る舞い、ナノ粒子同士の凝集、クラスター核発生、成長、さらには再配列によるメソ結晶（ナノ粒子からなる結晶）を形成する過程を明らかにし、その時定数も評価している。

第５章では、有機無機ハイブリッドナノ粒子に適したプロセス提案を行っている。有機修飾分子存在下で反応速度が低い場合、反応器の長さは長くなり設備コストは増大するが、高温水との混合による急速昇温が必要ないため、高い熱回収効率が達成でき運転コストは削減できることを指摘している。

第６章は総括であり、本論分で得られた成果をまとめている。

以上、本論文は、超臨界水熱合成 in-situ 有機修飾プロセスにおける速度論と溶媒効果を初めて論じ、またナノ粒子形成直後の分散凝集・再配列挙動の追跡を通してナノ粒子の分子性を示唆するとともに、これらの知見に基づきプロセス設計指針を示したものであり、超臨界水熱合成プロセスの発展、ならびに、超臨界流体反応工学の発展に大きく寄与するものである。

よって、本論文は博士（工学）の学位論文として合格と認める。